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(19) (CA) **CANADIAN PATENT** (12)

(54) **Hydrophilized Support Materials for Offset Printing  
Plates**

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leaving a residue, in order to produce hydrophilic non-image areas.

- 5       -     The support bared in the non-image areas must have a high affinity for water, i.e. must be highly hydrophilic, so that, in the lithographic printing process, it absorbs water rapidly and durably and has a sufficiently repellent action on the greasy printing ink.
- 10       -     There must be a sufficient degree of adhesion of the light-sensitive layer before exposure and of the printing areas of the layer after exposure.

15       Foil of aluminum, steel, copper, brass or zinc and also plastic sheets or paper can be used as the base material for such supports. These raw materials are converted by suitable operations such as, for example, graining, mattchromium plating, superficial oxidation and/or application of an interlayer  
20       into supports for offset printing plates. Aluminum, which nowadays is presumably the most widely used base material for offset printing plates, is superficially roughened according to known methods by dry brushing, wet brushing, sandblasting or chemical and/or  
25       electrochemical treatment. To improve the abrasion resistance, the roughened substrate can also be subjected to an anodizing step in order to build up a thin oxide layer.

30       In practice, the support materials, in particular anodically oxidized support materials based on aluminum, are frequently subjected to a further treatment step before the application of a light-sensitive layer, in order to improve the layer adhesion, to intensify the hydrophilic character and/or to facili-

tate the development of the light-sensitive layers; these steps include, for example, the following methods:

5 In U.S. Patent No. 2,714,066, U.S. Patent No. 3,181,461 and U.S. Patent No. 3,280,734 or U.S. Patent No. 3,902,976, processes for the hydrophilizing of printing plate support materials based on aluminum which may have been anodically oxidized are described, wherein these materials are treated with an aqueous  
10 sodium silicate solution with or without applying an electric current.

It is known from U.S. Patent No. 3,276,868 and U.S. Patent No. 4,153,461 to use polyvinylphosphonic acid or copolymers based on vinylphosphonic acid, acrylic acid and vinyl acetate for the hydrophilizing of  
15 printing plate support materials based on aluminum which may have been anodically oxidized. The use of salts of these compounds is also mentioned, but not specified in more detail.

20 The use of complex fluorides of titanium, zirconium or hafnium according to U.S. Patent No. 3,440,050 likewise leads to additional hydrophilizing of aluminum oxide layers on printing plates support materials.

25 In addition to these hydrophilizing methods which have become particularly widely known, the use of the following polymers in this field of application has also been described, for example:

30 In German Auslegeschrift No. 1,056,931, the use of water-soluble, linear copolymers based on alkyl vinyl ethers and maleic anhydrides in light-sensitive layers for printing plates is described. Amongst these copolymers, those are particularly hydrophilic in which the maleic anhydride component was not reacted,  
35 or more or less completely reacted, with ammonia, an alkali metal hydroxide or an alcohol.

German Auslegeschrift No. 1,091,433 (equivalent to British Patent No. 815,471) has disclosed the hydrophilizing of printing plate support materials based on metals by means of film-forming organic polymers such as polymethacrylic acid or sodium carboxymethylcellulose or sodium hydroxyethylcellulose on aluminum supports or with a copolymer of methyl vinyl ether and maleic anhydride on magnesium supports.

For the hydrophilizing of printing plate support materials of metals, initially water-soluble polyfunctional amino/urea/aldehyde synthetic resins or sulfonated urea/aldehyde synthetic resins, which are cured on the metal support in a water-insoluble state, are used according to German Auslegeschrift No. 1,173,917 (equivalent to British Patent No. 907,718).

For preparing a hydrophilic layer on printing plate support materials according to U.S. Patent No. 3,232,783, a) an aqueous dispersion of a modified urea/formaldehyde resin, an alkylated methylolmelamine resin or a melamine/formaldehyde/polyalkylenepolyamine resin is first applied to the support, then b) an aqueous dispersion of a polyhydroxy or polycarboxy compound, such as sodium carboxymethylcellulose, is applied and finally the base so coated is treated c) with an aqueous solution of a Zr, Hf, Ti or Th salt.

In U.S. Patent No. 2,991,204, a copolymer which, in addition to acrylic acid, acrylate, acrylamide or methacrylamide units, also contains Si-trisubstituted vinylsilane units is described as a hydrophilizing agent for printing plate support materials.

The use of polyacrylic acid as a hydrophilizing agent for printing plate support materials of aluminum, copper or zinc is known from U.S. Patent No. 3,298,852.

The hydrophilic layer on a printing plate sup-

port material according to U.S. Patent No. 3,733,200 is formed from a water-insoluble hydrophilic acrylate or methacrylate homopolymer or copolymer with a water absorption of at least 20% by weight.

5 In German Auslegeschrift No. 2,305,231 (equivalent to British Patent No. 1,414,575), hydrophilizing of printing plate support materials is described, wherein a solution or dispersion of a mixture of an aldehyde and a synthetic polyacrylamide is  
10 applied to the support.

U.S. Patent No. 3,861,917 has disclosed hydrophilizing of roughened and anodically oxidized aluminum printing plate supports by means of ethylene or methyl vinyl ether/maleic anhydride copolymers,  
15 polyacrylic acid, carboxymethylcellulose, sodium poly-(vinylbenzene-2,4-disulfonate) or polyacrylamide.

In U.S. Patent No. 3,860,426, a hydrophilic adhesion layer for aluminum offset printing plates is described, which is located between the anodically oxidized surface of the printing plate support and the  
20 light-sensitive layer and, in addition to a cellulose ether, also contains a water-soluble Zn, Ca, Mg, Ba, Sr, Co or Mn salt. The layer weight of cellulose ether in the hydrophilic adhesion layer is 0.2 to 1.1 mg/dm<sup>2</sup>,  
25 and the same layer weight is also given for the water-soluble salts. The mixture of cellulose ether and salt is applied in an aqueous solution, if appropriate with addition of an organic solvent and/or a surfactant, to the support.

30 Aqueous solutions of acrylic acid, polyacrylic acid, polymethacrylic acid, polymaleic acid or copolymers of maleic acid with ethylene or vinyl alcohol are used according to U.S. Patent No. 3,672,966 for compacting anodically oxidized aluminum surfaces after  
35 they have been sealed, in order to avoid seal deposits.

The hydrophilizing agents for printing plate

support materials according to U.S. Patent No. 4,049,746 contain salt-like reaction products of water-soluble polyacrylic resins with carboxyl groups and polyalkyleneimine/urea/aldehyde resins.

In British Application No. 1,246,696, published September 15, 1971, hydrophilic colloids such as hydroxyethyl-cellulose, polyacrylamide, polyethylene oxide, polyvinylpyrrolidone, starch or gum arabic are described as hydrophilizing agents for anodically oxidized aluminum printing plate supports.

Japanese Patent Application No. 64/23,982 published October 27, 1964, has disclosed hydrophilizing of metal printing plate supports with polyvinylbenzenesulfonic acid.

In the state of the art, the use of those metal complexes for hydrophilizing printing plate support materials has also been disclosed which contain low-molecular ligands; these include, for example:

- Complex ions of divalent or polyvalent metal cations and ligands such as ammonia, water, ethylenediamine, nitrogen oxide, urea or ethylenediaminetetraacetate, according to U.S. Patent No. 4,208,212,
- iron cyanide complexes such as  $K_4[Fe(CN)_6]$  or  $Na_3[Fe(CN)_6]$  in the presence of heteropolyacids such as phosphomolybdic acid or its salts and of phosphates, according to U.S. Patent No. 3,769,043 or/and U.S. Patent No. 4,420,549, or

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- iron cyanide complexes in the presence of phosphates and complex formers such as ethylenediaminetetraacetic acid for electrophotographic printing plates with a zinc oxide surface, according to U.S. Patent No. 3,672,885.

6a

A



U.S. Patent No. 4,427,765 describes a process in which salts of polyvinylphosphonic acids, polyvinylsulfonic acids, polyvinylmethylphosphinic acids and other polyvinyl compounds are used as post-treatment agents.

In U.S. Patent No. 4,214,531, a process for treating image-bearing offset printing plates with polyacrylamide or a mixture of polyacrylamide and polyacrylic acid is used.

A copolymer of acrylamide and vinyl monomers is used in USSR No. 647,142 for hydrophilizing offset printing plates.

In German Patent No. 2,615,075 (equivalent to British Patent No. 1,495,895), a polyacrylamide is used for the same purpose.

German Patent No. 1,091,433 describes a process for the post-treatment of offset printing plate supports with polymers of methacrylic acid, methyl vinyl ether and maleic anhydride.

Acrylamide for the treatment of printing plate supports is also mentioned in German Offenlegungsschrift No. 2,540,561.

For the same purpose, in particular for improving the storage stability of printing plates, German Offenlegungsschrift No. 2,947,708 describes inter alia Ni salt solutions of acrylamide and acrylic acid as well as acrylamide and vinylpyrrolidone.

All the methods described above, however, involve more or less serious disadvantages so that the support materials produced in this way frequently no longer meet the current requirements of offset printing:

- Thus, after the treatment with alkali metal silicates, which lead to good developing properties and hydrophilic character, a certain deterioration in the

storage stability of light-sensitive layers applied thereto must be accepted.

- Although the complexes of transition metals promote in principle the hydrophilic character of anodically oxidized aluminum surfaces, they have the disadvantage of being very readily soluble in water, so that they can easily be removed when the layer is developed with aqueous developer systems which of late increasingly contain surfactants and/or chelate formers which have a high affinity to these metals. As a result, the concentration of the transition metal complexes on the surfaces is reduced to a greater or lesser extent, and this can lead to a weakening of the hydrophilic effect.

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- In the treatment of supports with water-soluble polymers, the good solubility of the latter, particularly in aqueous-alkaline developers, such as are predominantly used for the development of positive-working light-sensitive layers, also leads to a marked weakening of the hydrophilizing effect.

20

25
- In polymers containing acid groups, an adverse effect arises since free anionic acid groups can interact with the diazo cations of negative-working light-sensitive layers, so that a marked dye stain due to retained diazo compounds remains after development on the non-image areas.

30

5           -     The combination of a mixture of a water-soluble polymer, such as a cellulose ether, and a water-soluble metal salt also leads, since the layer weights and hence the layer thickness are selected to be relatively high (German Auslegeschrift No. 2,364,177), to reduced layer adhesion which can manifest itself, for example, in disbonding of image areas by parts of the developer liquid during development.

10

#### SUMMARY OF THE INVENTION

It is accordingly an object of the invention to provide support materials for offset printing plates having good hydrophilizing properties.

15           It is another object of the invention to provide support materials, as above, which are equally suitable as supports for positive-working, negative-working or electrophotographic light-sensitive layers.

20           It is yet another object of the invention to provide support materials, as above, which have good storage stability.

25           It is still another object of the invention to provide support materials, as above, in which no reactions occur between a hydrophilizing agent and the light-sensitive layer, and which do not reduce the layer adhesion.

30           These objects are achieved by a support material for offset printing plates, which comprises an aluminum-containing base material, and a hydrophilic coating applied to at least one side of the aluminum containing base material, the hydrophilic coating comprising a phosphonic acid compound selected from the group consisting of a polymer of acrylamidoisobutylene phosphonic acid, a copolymer of acrylamide and acrylamidoisobutylene-

phosphonic acid, a salt of either of the above with an at least divalent metal cation, and combinations of any of the above.

The objects of the invention are also achieved  
 5 by a process for the preparation of a support material for offset printing plates which comprises coating an aluminum-containing base material, with the above-described phosphonic acid compound, the phosphonic acid compound being in the form of an aqueous solution having a  
 10 concentration of from about 0.02 to about 5.0% by weight, and drying the layer. The coating step is performed by dipping or electrochemical treatment.

When the phosphonic acid compound is a polymer or copolymer salt, the coating process can be performed  
 15 in two steps, in which the polymer or copolymer is coated onto the aluminum-containing base material, followed by treating the base material with a solution of the metal cation salt which reacts with the polymer or copolymer coating.

#### 20 DETAILED DESCRIPTION OF THE PREFERRED EMOBODIMENTS

The invention starts from a support material in the form of plates, sheets or webs for offset printing plates, composed of aluminum, which may have been pretreated, or one of its alloys carrying on at  
 25 least one side a hydrophilic coating of a phosphonic acid compound.

The distinctive feature is that the hydrophilic coating comprises a) a polymer of ~~acrylamidoisobutylenephosphonic acid~~ or b) a copolymer of acrylamide and acrylamidoisobutylenephosphonic acid ~~or~~ c) a salt  
 30 of a) or b) with an at least divalent metal cation. In the case of the copolymers of b) and the copolymer salts of c), the acrylamide/acrylamidoisobutylene phosphonic acid ratio is between about 99:1 and about

1:99 on a molar basis, and preferably between about 3:97 and about 90:10 on a molar basis.

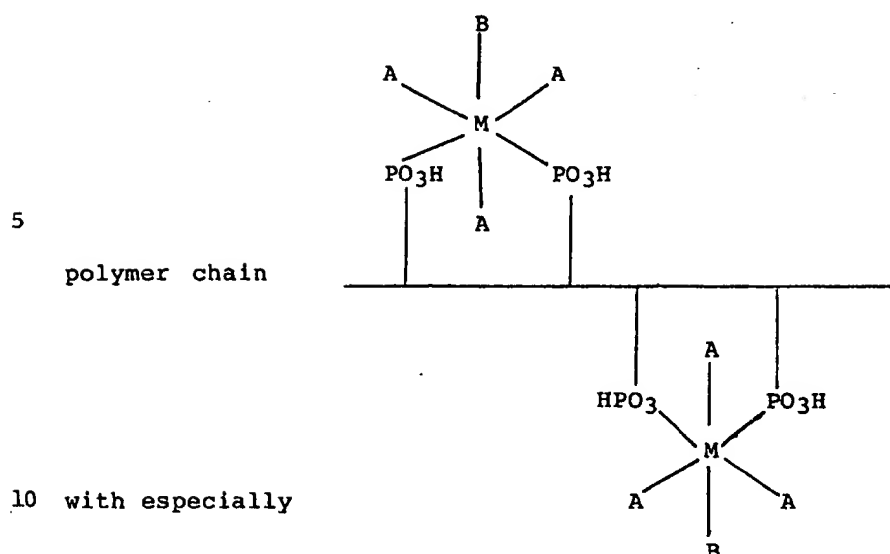
In the copolymeric salts, 1 to 3, preferably 2, coordination sites of the metal cation are occupied by the functional groups of the polymer.

To prepare the reaction products of the variants c), the metal cations are in general used in the form of their salts with mineral acid anions or as acetates; the divalent, trivalent or tetravalent cations, in particular the divalent cations, are preferred here. The cations are especially  $V^{5+}$ ,  $Bi^{3+}$ ,  $Al^{3+}$ ,  $Fe^{3+}$ ,  $Zr^{4+}$ ,  $Sn^{4+}$ ,  $Ca^{2+}$ ,  $Ba^{2+}$ ,  $Sr^{2+}$ ,  $Mn^{3+}$ ,  $Co^{2+}$ ,  $Fe^{2+}$ ,  $Mn^{2+}$ ,  $Ni^{2+}$ ,  $Cu^{2+}$ ,  $Zn^{2+}$  or  $Mg^{2+}$  ions.

These reaction products can be prepared in a simple manner in aqueous solutions at temperatures of from about 20 to about 100°C, preferably at from about 25 to about 40°C. The metal salt dissolved in water, or if necessary dissolved in dilute mineral acid, is slowly added dropwise to the aqueous polymer solution. The conversion of the reaction components to the products described above then starts immediately. The rapid start of the reaction manifests itself - as a function of the metal cation used - in the immediate onset of a color change of the solution or by the formation of a precipitate.

For purification, the products can be precipitated by neutralizing the reaction solution with dilute alkali metal hydroxide or ammonia solutions, the unconverted starting products remaining in the solution. The yields of these reactions are over 90%. It is also possible, instead of the acid forms of the polymers, as described, to employ their salt forms with a monovalent cation, such as a sodium or ammonium salt.

The chemical structure of the polymer/metal complexes according to the invention can be represented as follows:



M = a central ion and,  
 in the case of 2-valent metal cations,  $A = B = H_2O$   
 or, in the case of 3-valent metal cations  $A = H_2O$   
 15 and  
 $B = NO_3^-$ ,  $Cl^-$ ,  $HSO_4^-$ ,  $H_2PO_4^-$ ,  $CH_3COO^-$ ,  $OH^-$  or similar  
 anions.

Such complexes are formed in particular when  
 the polymer solution is slowly added to an excess of  
 20 the metal salt.

For treating the aluminum surface for the pre-  
 preparation of the support materials according to the  
 invention for offset printing plates, the aqueous solu-  
 tions of the copolymers are employed in concentrations  
 25 of from about 0.02 to about 5% by weight, preferably in  
 concentrations of from about 0.1 to about 1% by weight.

For treating the substrates for the prepara-  
 tion of the support materials according to the inven-  
 tion for offset printing plates with the salts of the  
 30 copolymers, the isolated and dried reaction products  
 are preferably dissolved in solutions of from about 0.1

to about 10% by weight mineral acids, in particular, solutions of from about 0.5 to about 3% by weight mineral acids, preferably phosphoric acid, in concentrations of from about 0.05 to about 5% by weight in particular in concentrations of from about 0.1 to about 1% by weight.

The treatment of these substrates with these solutions is advantageously carried out by dipping the formats or by passing the substrate web through a bath of these solutions. Temperatures from about 20 to about 95°C, preferably from about 25 to about 60°C, and residence times from about 2 seconds to about 10 minutes, preferably from about 10 seconds to about 3 minutes, prove to be the most suitable for use in practice. An increase in the bath temperature accelerates the chemisorption of the copolymers and the polymer metal complexes on the substrate. This allows a considerable reduction of the residence times, in particular in the case of continuous web treatment. The dipping treatment is then advantageously followed by a rinsing step with water. The substrate thus treated is then dried, advantageously at temperatures from about 110 to about 130°C.

The treatment of the aluminum substrate with the salts of the copolymers can also be carried out as a two-stage process. In this case, the substrate is dipped in the first step, for example, into an about 0.01 to about 10%, preferably about 0.1 to about 5%, aqueous solution of the starting polymer. Without prior rinsing or drying, the substrate can then be transferred into a second bath which contains an about 0.1% to saturated, preferably about 0.5 to about 10%, aqueous salt solution with the above-mentioned polyvalent metal ions. Rinsing and drying is carried out as in the one-stage process. In the two-stage treatment, the reaction products described above are formed on the

substrate during the treatment. Using this process variant, even the trivalent metal ion reaction products sparingly soluble in strongly acidic media can be applied to the substrate.

5 A determination of the weight of the hydrophilic coating applied raises problems, since even small quantities of the applied product show marked effects and are relatively strongly anchored in and on the surface of the support material. It can be assumed,  
10 however, that the quantity applied is significantly below  $0.1 \text{ mg/dm}^2$ , in particular below  $0.08 \text{ mg/dm}^2$ .

The support materials according to the invention, thus prepared, can then be coated with various light-sensitive layers for the production of offset  
15 printing plates.

Suitable substrates for the preparation of the support materials according to the invention include those of aluminum or one of its alloys. These include, for example:

20 - "pure aluminum" (DIN material No. 3.0255), i.e. composed of  $\geq 99.5\%$  of Al and the following permissible impurities of (total  $0.5\%$  maximum)  $0.3\%$  of Si,  $0.4\%$  of Fe,  $0.03\%$  of Ti,  $0.02\%$  of Cu,  $0.07\%$  of  
25 Zn and  $0.03\%$  of others, or

"Al alloy 3003" (comparable with DIN material No. 3.0515), i.e. composed of  $\geq 98.5\%$  of Al, 0 to  $0.3\%$  of Mg and 0.8 to  
30 1.5% of Mn as the alloy constituents and the following permissible impurities of  $0.5\%$  of Si,  $0.5\%$  of Fe,  $0.2\%$  of Ti,  $0.2\%$  of Zn,  $0.1\%$  of Cu and

0.15% of others.

35 However, the process according to the invention can also be transferred to other aluminum alloys.



The aluminum support materials for printing plates, as very frequently encountered in practice, are in general also roughened mechanically (for example by brushing and/or abrasive treatments), chemically (for example by etching) or electrochemically (for example by an alternating current treatment in aqueous HCl or HNO<sub>3</sub> solutions), before the light-sensitive layer is applied. For the present invention, aluminum printing plates with electrochemical roughening are used especially.

In general, the process parameters in the roughening stage are within the following ranges: the temperature of the electrolyte between about 20 and about 60°C, the concentration of active substance (acid, salt) between about 5 and about 100 g/l, the current density between about 15 and about 130 A/dm<sup>2</sup>, the residence time between about 10 and about 100 seconds and the electrolyte flow velocity on the surface of the workpiece to be treated between about 5 and about 100 cm/second; the current type used is in most cases alternating current, but modified current types, such as an alternating current with different amplitudes of current intensity for the anode current and cathode current are also possible.

The mean peak-to-valley height  $R_z$  of the roughened surface then is in the range from about 1 to about 15  $\mu\text{m}$ , in particular in the range from about 4 to about 8  $\mu\text{m}$ .

The peak-to-valley height is determined in accordance with DIN 4768 (October 1970 edition), and the peak-to-valley height  $R_z$  is then the arithmetic mean of the individual peak-to-valley heights for five continuous individual measurement sections. The individual peak-to-valley height is defined as the distance of the two parallels to the center line, which touch the roughness profile at the highest and lowest point

respectively within the individual measurement sections. The individual measurement section is the fifth part of the length, projected perpendicularly onto the center line, of that part of the roughness profile which is used directly for evaluation. The center line is the line parallel to the general direction of the roughness profile of the form of the geometrically ideal profile, which line divides the roughness profile such that the sums of the areas filled with material above it and of the areas free of material below it are equal.

The electrochemical roughening process is then followed, in a further process stage which may have to be applied, by an anodic oxidation of the aluminum, for example in order to improve the abrasion and adhesion properties of the surface of the support material. The conventional electrolytes such as  $H_2SO_4$ ,  $H_3PO_4$ ,  $H_2C_2O_4$ , amidosulfonic acid, sulfosuccinic acid, sulfosalicylic acid or mixtures thereof can be used for the anodic oxidation. Reference is made, for example, to the following standard methods for the use of aqueous electrolytes containing  $H_2SO_4$  in the anodic oxidation of aluminum (in this connection, see, for example, B.M. Schenk, Werkstoff Aluminium und seine anodische Oxydation [The material aluminum and its anodic oxidation], Francke Verlag - Berne, 1948, page 760; Praktische Galvanotechnik [Electroplating Practice], Eugen G. Leuze Verlag - Saulgau, 1970, pages 395 et seq. and pages 518/519; W. Hübner and C.T. Speiser, Die Praxis der anodischen Oxydation des Aluminiums [Practice of the anodic oxidation of aluminum], Aluminium Verlag - Düsseldorf, 1977, 3rd edition, pages 137 et seq.):

- The direct-current sulfuric acid process, in which the anodic oxidation is carried out for 10 to 60 minutes in an aqueous

electrolyte of usually about 230 g of  $\text{H}_2\text{SO}_4$  per 1 liter of solution at 10 to 22°C and a current density of 0.5 to 2.5 A/dm<sup>2</sup>. The sulfuric acid concentration in the aqueous electrolyte solution can here also be reduced to 8 to 10% by weight of  $\text{H}_2\text{SO}_4$  (about 100 g of  $\text{H}_2\text{SO}_4$ /l) or increased to 30% by weight (365 g of  $\text{H}_2\text{SO}_4$ /l) and higher.

- The "hard anodizing" is carried out with an aqueous electrolyte, containing  $\text{H}_2\text{SO}_4$ , of a concentration of 166 g of  $\text{H}_2\text{SO}_4$ /l (or about 230 g of  $\text{H}_2\text{SO}_4$ /l) at an operating temperature of 0 to 5°C, at a current density of 2 to 3 A/dm<sup>2</sup>, a rising voltage of about 25 to 30 V at the start and about 40 to 100 V toward the end of the treatment and for 30 to 200 minutes.

In addition to the processes, already mentioned in the preceding paragraph, for the anodic oxidation of printing plate support materials, the following processes can also be used, for example: the anodic oxidation of aluminum in an electrolyte which contains aqueous  $\text{H}_2\text{SO}_4$  and the  $\text{Al}^{3+}$  ion content of which is adjusted to values of more than 12 g/l (according to U.S. Patent No. 4,211,619), in an aqueous electrolyte containing  $\text{H}_2\text{SO}_4$  and  $\text{H}_3\text{PO}_4$  (according to U.S. Patent No. 4,049,504) or in an aqueous electrolyte containing  $\text{H}_2\text{SO}_4$ ,  $\text{H}_3\text{PO}_4$  and  $\text{Al}^{3+}$  ions (according to U.S. Patent No. 4,229,226).

Direct current is preferably used for the anodic oxidation, but alternating current or a combination of these current types (for example direct current with a superposed alternating current) can also be used. The aluminum oxide layer weights are in the range of

from about 1 to about 10 g/m<sup>2</sup>, corresponding to a layer thickness of from about 0.3 to about 3.0  $\mu$ m.

Suitable light-sensitive layers are in principle all those which, after exposure, if appropriate with subsequent development and/or fixing, give an imagewise surface, which can be used for printing. They are applied to one of the conventional support materials either by the manufacturer of presensitized printing plates or directly by the user.

In addition to the layers which contain silver halides and are used in many fields, various other layers are also known, such as are described, for example, in "Light-Sensitive Systems" by Jaromir Kosar, published by John Wiley & Sons, New York 1965: colloid layers containing chromates and dichromates (Kosar, chapter 2); layers which contain unsaturated compounds and in which these compounds are isomerized, rearranged, cyclized or crosslinked on exposure (Kosar, chapter 4); layers which contain photopolymerizable compounds and in which monomers or prepolymers polymerize on exposure, if appropriate by means of an initiator (Kosar, chapter 5); and layers containing o-diazo-quinones, such as naphthoquinone-diazides, p-diazo-quinones or diazonium salt condensates (Kosar, chapter 7). The suitable layers also include electrophotographic layers, that is to say layers which contain an inorganic or organic photoconductor. In addition to the light-sensitive substances, these layers can of course also contain further constituents such as, for example, resins, dyes or plasticizers.

In particular, the following light-sensitive compositions or compounds can be used for coating the support materials prepared by the process according to the invention:

Positive-working o-quinone-diazone compounds, preferably o-naphthoquinone-diazone compounds, which

are described, for example, in German Patent Nos. 854,890, 865,109, 879,203, 894,959, 938,233, 1,109,521, 1,144,705, 1,118,606, 1,120,273 and 1,124,817.

Negative-working condensation products of aromatic diazonium salts and compounds with active carbonyl groups, preferably condensation products of diphenylaminediazonium salts and formaldehyde, which are described, for example, in German Patent Nos. 596,731, 1,138,399, 1,138,400, 1,138,401, 1,142,871 and 1,154,123, U.S. Patent Nos. 2,679,498 and 3,050,502 and British Published Application No. 712,606.

Negative-working, mixed condensation products of aromatic diazonium compounds, for example according to German Offenlegungsschrift No. 2,024,244, which contain at least one unit each of the general types A(-D)<sub>n</sub> and B, linked by a divalent bridge member derived from a carbonyl compound capable of condensation. These symbols are here defined as follows: A is the radical of a compound which contains at least two aromatic carbocyclic and/or heterocyclic nuclei and which is capable of condensation in an acid medium with an active carbonyl compound in at least one position. D is a diazonium salt group bonded to an aromatic carbon atom of A; n is an integer from 1 to 10 and B is the radical of a compound which is free of diazonium groups and which is capable of condensation in an acid medium with an active carbonyl compound in at least one position of the molecule.

Positive-working layers according to German Offenlegungsschrift No. 2,610,842, which contain a compound which eliminates acid on irradiation, a compound with at least one C-O-C group which can be eliminated by acid (for example an orthocarboxylic acid ester group or a carboxylic acid amide-acetal group) and, if appropriate, a binder.

Negative-working layers of photopolymerizable

monomers, photoinitiators, binders and, if appropriate, further additives. The monomers used here are, for example, acrylates and methacrylates or reaction products of diisocyanates with partial esters of polyhydric alcohols, such as are described, for example, in 5 U.S. Patents No. 2,760,863 and No. 3,060,023 and in German Offenlegungsschriften No. 2,064,079 and No. 2,361,041. Suitable photoinitiators are inter alia benzoin, benzoin ethers, polynuclear quinones, acridine 10 derivatives, phenazine derivatives, quinoxaline derivatives, quinazoline derivatives or synergistic mixtures of different ketones. A large variety of soluble organic polymers can be used as the binders, for example polyamides, polyesters, alkyd resins, polyvinyl alcohol, 15 polyvinylpyrrolidone, polyethylene oxide, gelatine or cellulose ethers.

Negative-working layers according to German Offenlegungsschrift No. 3,036,077 which contain, as the 20 light-sensitive compound, a diazonium salt polycondensation product or an organic azido compound and, as the binder, a high-molecular polymer with alkenylsulfonyl- or cycloalkenylsulfonyl-urethane side groups.

Photo-semiconducting layers, such as are described, for example, in German Patents No. 1,117,391, 25 No. 1,522,497, No. 1,572,312, No. 2,322,046 and No. 2,322,047, can also be applied to the support materials, whereby highly light-sensitive electrophotographic layers are produced.

The coated offset printing plates obtained 30 from the support materials according to the invention are converted into the desired printing form in the known manner by imagewise exposure or irradiation and washing out of the non-image areas with a developer, preferably an aqueous developer solution. Surprisingly, 35 offset printing plates, the base support materials of which were treated according to the inven-

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tion, are distinguished from those plates which for comparison were treated with a homopolymeric acrylamide, with polymeric vinylphosphonic acid or only with hot water, by a markedly lower dye stain and an improved hydrophilic character. The adhesion of the light-sensitive layer to the surface of the support was also better in the samples treated according to the invention than in the comparison samples.

Examples A of the preparation of a roughened and anodized printing plate support

5           A1:     Bright-rolled aluminum strip (DIN material No. 3.0255) of 0.3 mm thickness was degreased with an aqueous alkaline 2% pickling solution at an elevated temperature of about 50 to 70°C. The electrochemical roughening of the aluminum surface was effected with alternating current and in an electrolyte containing HNO<sub>3</sub>. This gave a surface roughness with an R<sub>z</sub> value of 6 /μm. The subsequent anodic oxidation was carried out according to the process described in German Offenlegungsschrift No. 2,811,396 in an electrolyte containing sulfuric acid. The oxide weight was about 3.0 g/m<sup>2</sup>. A support prepared in this way is marked by the number 1 in Tables 2 and 3.

20           The aluminum strip prepared in the above manner was then passed through a warm bath (60°C) of a 0.5% solution which contained one of the polymers according to the invention or one of the comparison substances (N1 to NV13). The compositions of these solutions are listed in Table 1. The residence time in the bath was 30 seconds. In a rinsing step, the excess solution was then removed with tap water and the strip was dried with hot air at temperatures between 100 and 130°C.

30           A2:     Bright-rolled aluminum strip (DIN material No. 3.0515) of 0.3 mm thickness was degreased with an aqueous alkaline 2% pickling solution at an elevated temperature of about 50 to 70°C. Electrochemical roughening of the aluminum surface was effected with alternating current



and in an electrolyte containing hydrochloric acid. This gave a surface roughness with an  $R_z$  value of 6  $\mu\text{m}$ . The subsequent anodic oxidation was carried out in accordance with the process described in German Offenlegungsschrift No. 2,811,396, and in an electrolyte containing sulfuric acid. The oxide weight was about 3.0  $\text{g}/\text{m}^2$ .

A support prepared in this way is marked by the number 2 in Tables 2 and 3.

The aluminum strip thus prepared was then passed through a warm bath ( $50^\circ\text{C}$ ) of a 0.5% solution which contained one of the polymers according to the invention or one of the comparison substances (N1 to NV13). The compositions of these solutions are listed in Table 1.

A3: Bright-rolled aluminum strip (DIN material No. 3.0255) of 0.2 mm thickness was degreased with an aqueous-alkaline 2% pickling solution at an elevated temperature of about 50 to  $70^\circ\text{C}$ . The support was then brushed, using cutting graining agents. This gave a surface roughness with an  $R_z$  value of 4  $\mu\text{m}$ . The subsequent anodic oxidation was carried out according to U.S. Patent No. 3,511,661 in an electrolyte containing phosphoric acid. The oxide weight was 0.9  $\text{g}/\text{m}^2$ .

The aluminum strip thus treated was cut into sheets of 50 x 45 cm size.

A support prepared in this way is marked by the number 3 in Tables 2 and 3.

5           The supports thus prepared were dipped into a warm bath (60°C) of an aqueous solution of 0.4% of one of the polymers listed under N1 to NV13 in Table 1. The residence time in the bath was 60 seconds. The excess solution was then removed in a rinsing step with deionized water and the support was dried in air.

Example B of the preparation of the reaction products (polymer/metal complexes)

10           0.2 mol, relative to one phosphonic acid unit, of the polymer listed under N3 in Table 1 was dissolved in 600 ml of water. 0.2 mol of  $\text{Co}(\text{NO}_3)_2$  dissolved in 200 ml of water was then slowly added dropwise to this solution. After the addition had ended, the mixture  
15 was stirred for one additional hour. The reaction solution was then neutralized by slowly adding dilute aqueous NaOH solution. While doing this, the cobalt complex was deposited quantitatively as a viscous, rubber-like violet-colored precipitate. This precipitate was filtered  
20 off, washed with water and then with methanol and dried at 60°C in a drying oven. The excess  $\text{Co}_2^+$  ions remained in the filtrate. The polymers could also be reacted in the same way with other, at least divalent metal cations.

Table 1

	1 No.	2 Composition	3 Monomer ratio
5	N1	p-AMIP*/AM**	1:99
	N2	"	3:97
	N3	"	10:90
10	N4	"	50:50
	N5	"	70:30
	N6	p-AMIP*	100: 0
	N7	p-AMIP/AM-Ca***	3:97
15	N8	p-AMIP/AM-Sr***	10:90
	N9	p-AMIP/AM-Co***	10:90
	N10	p-AMIP/AM-Mg***	1:99
	NV11	water	
20	NV12	p-VPS	
	NV13	AM	

The meanings of the abbreviations are:

- 25 \* acrylamidoisobutylenephosphonic acid  
 \*\* acrylamide  
 \*\*\* metal salts (Ca, Sr, Mg or Co) of the copolymeric acid, prepared according to Example B  
 p polymer

The support materials described under A1 to A3, which were each treated with 13 different solutions, gave a total of 39 post-treated supports. They are listed in Table 2, together with the measurement results explained below.

In addition to the dipping treatment described under A1 and A3, some supports were subjected to an electrochemical post-treatment, which is described below.

#### 10 Example C of electrochemical treatment

Supports from Example A2 were dipped at 40°C into a 0.2% solution of the products N1 to NV12 (Table 1). The supports were connected as the anode and treated for 20 seconds with direct current at 10 V. During this treatment, the current fell from initially 3 A/dm<sup>2</sup> to 0.2 A/dm<sup>2</sup>. Subsequently, the excess solution was removed in a rinsing step with deionized water, and the supports were dried in air. The supports thus prepared and the results of the measurements described below are listed in Table 3.

The following measurements were carried out on each of the support materials obtained according to the examples:

Testing of the alkali resistance of the surface  
25 (according to U.S. Patent No. 3,940,321, columns 3 and 4, lines 29 to 68 and lines 1 to 8):

The measure of the alkali resistance of an aluminum oxide layer is the rate of dissolution of the layer in seconds in an alkaline zincate solution. The layer is the more alkali-resistant, the longer it takes to dissolve it. The layer thicknesses should be approximately comparable, since they naturally also represent a parameter for the rate of dissolution. A drop of a solution of 500 ml of distilled H<sub>2</sub>O, 480 g of

KOH and 80 g of zinc oxide is applied to the surface to be investigated and the time to the appearance of metallic zinc is determined, which manifests itself by a black coloration of the investigated spot. This "zincate test" is mentioned in column 4 of Table 2.

Testing of the hydrophilic character of the support materials prepared according to the invention

The test is carried out by means of measurements of the angle of contact with a water drop placed on top. In this test, the angle between the support surface and a tangent going through the point of contact of the drop is measured. The angle is in general between 0° and 90°. The wetting is the better, the smaller the angle. The data in column 5 of Table 2 relate to these contact angle measurements.

Examples D of coating of the supports with light-sensitive materials

D1: A piece of each of the supports described in the support examples A1 to A3 was coated with the following solution:

6.6	p.b.w.	of a cresol/formaldehyde novolac (having a softening range of 105° - 120°C according to DIN 53 181)
1.1	p.b.w.	of 4-(2-phenyl-prop-2-yl)-phenyl naphtho-1,2-quinone-2-diazide-4-sulfonate,
0.6	p.b.w.	of 2,2'-bis-(naphtho-1,2-quinone-2-diazide-5-sulfonyloxy)-1,1'-dinaphthylmethane,
0.24	p.b.w.	of naphtho-1,2-quinone-2-diazide-4-sulfochloride,
0.08	p.b.w.	of crystal violet and
91.36	p.b.w.	of a solvent mixture of 4

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5 parts by volume of ethylene glycol monomethyl ether, 5 parts by volume of tetrahydrofuran and 1 part by volume of butyl acetate.

The coated supports were dried in a drying tunnel at temperatures of up to 120°C. The printing plates thus prepared were exposed under a positive original and developed with a developer of the following composition:

10	5.3	p.b.w.	of sodium metasilicate x 9 H <sub>2</sub> O
	3.4	p.b.w.	of trisodium phosphate x 12 H <sub>2</sub> O
15	0.3	p.b.w.	of sodium dihydrogen phosphate (anhydrous) and
	91.0	p.b.w.	of water.

The printing forms obtained were visually assessed for any dye residues (blue stain) still present in the non-image areas. The result is given in column 6 of Table 2.

D2: A piece of each of the supports described in the support examples A1 to A3 was provided with the following negative-working light-sensitive layer:

25	16.75	p.b.w.	of an 8% solution of the reaction product of a polyvinyl butyral, having a molecular weight of 70,000 to 80,000 and composed of 71% by weight of vinyl butyral, 2% of vinyl acetate and 27% by weight of vinyl alcohol units, with propenylsulfonyl
30			

		isocyanate,
5	2.14 p.b.w.	of 2,6-bis-(4-azido-benzal)- 4-methylcyclohexanone,
	0.23 p.b.w.	of Rhodamin <sup>®</sup> 6 GDN extra and
	0.21 p.b.w.	of 2-benzoylmethylene-1- methyl- $\beta$ -naphthothiazoline in
10	100 p.b.v.	of ethylene glycol monomethyl ether and
	50 p.b.v.	of tetrahydrofuran.

The supports were dried as described under 3.

The dry layer weight was 0.75 g/m<sup>2</sup>. The reproduction layer was exposed for 35 seconds under a negative original with a metal halide lamp of 5 kW power. The exposed layer was developed by means of a deep-etch pad with a developer solution of the following composition:

	5 p.b.w.	of sodium lauryl-sulfate
20	1 p.b.w.	of sodium metasilicate x 5 H <sub>2</sub> O and
	94 p.b.v.	of water.

The non-image areas of the printing forms obtained were visually assessed for any layer residues still present. The result of this assessment as compared with the state of the art (NV12) is to be found in column 7 of Table 2.

The meanings of the symbols in Table 2 are

- poorer than the state of the art of the comparison example of solution NV12
- o equally good as the state of the art of the comparison example of solution NV12
- + better than the state of the art of the comparison example of the solution NV12.

D3: To prepare an electrophotographically working offset printing plate, an anodically oxidized support prepared according to Example 15 of Table 2 was coated with the following solution:

5	10	p.b.w.	of 2,5-bis-(4'-diethylamino-phenyl)-1,3,4-oxadiazole,
	10	p.b.w.	of a copolymer of styrene and maleic anhydride, having a softening point of 210°C,
10	0.02	p.b.w.	Rhodamin <sup>®</sup> FB (C.I. 45 170) and
	300	p.b.w.	of ethylene glycol monomethyl ether

15 The supports were dried as described under 3.

The layer was negatively charged in the dark to about 400 V by means of a corona. The charged plate was exposed imagewise in a process camera and then developed with an electrophotographic suspension developer which represented a dispersion of 3.0 parts by weight of magnesium sulfate in a solution of 7.5 parts by weight of a pentaerythritol resin ester in 1200 parts by volume of an isoparaffin mixture having a boiling range from 185 to 210°C. After removal of the excess developer liquid, the developer was fixed and the plate was dipped for 60 seconds into a solution of

25	35	p.b.w.	of sodium metasilicate x 9 H <sub>2</sub> O,
	140	p.b.v.	of glycerol,
30	550	p.b.v.	of ethylene glycol and
	140	p.b.v.	of ethanol.

The plate was then rinsed with a vigorous jet of water, those areas of the photoconductor layer which are not covered with toner being removed. The plate was then ready for printing. The non-image areas of



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the plate showed a good hydrophilic character and indicated no signs of an attack even after the action of alkaline solutions. Several tens of thousands of good prints could be obtained with the printing form.

Table 2

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Ex- ample No.	2 Sup- port	3 Post-treat- ment agent	4 Zincate test time/sec.	5 Contact angle	6 Color stain 1)*	7 Layer residues 2)*
1	1	N1	o	+	-	-
2	-	N2	o	+	-	-
3	-	N3	o	+	-	-
4	-	N4	o	+	+	+
5	-	N5	o	+	+	+
6	-	N6	o	+	+	o
7	-	N7	o	+	+	o
8	-	N8	o	+	+	o
9	-	N9	o	+	+	o
10	-	N10	o	+	+	o
V11	-	NV11	o	-	-	-
V12	-	NV12	o	o	o	o
V13	-	NV13	-	-	-	-
14	2	N1	+	o	+	+
15	-	N2	o	o	+	+
16	-	N3	o	o	+	+
17	-	N4	o	+	+	+
18	-	N5	o	+	+	+
19	-	N6	o	+	+	o
20	-	N7	o	+	+	+
21	-	N8	o	+	+	o
22	-	N9	o	+	+	o
23	-	N10	o	o	+	o
V24	-	NV11	o	-	-	-
V25	-	NV12	o	o	o	o
V26	-	NV13	-	-	-	-
27	3	N1	+	+	+	+
28	-	N2	+	+	+	+
29	-	N3	+	+	+	+
30	-	N4	o	+	+	+
31	-	N5	o	+	+	+
32	-	N6	o	+	+	o
33	-	N7	o	+	+	o
34	-	N8	o	+	+	o
35	-	N9	o	+	+	o
36	-	N10	o	+	+	o
V37	-	NV11	o	-	-	-
V38	-	NV12	o	o	o	o
V39	-	NV13	o	-	-	-

1)\* for positive layers

2)\* for negative layers

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Table 2 proves that the products according to the invention are in many properties better than those of the state of the art, but not poorer in any of them.

Table 3

Ex- ample No.	Sup- port	Post- treatment agent	Zincate test time (sec)	Con- tact angle	Color stain 1)*	Layer residue 2)*
40	2	N1	+	+	+	+
41	2	N2	+	+	+	+
42	2	N3	+	o	+	+
43	2	N4	+	o	+	+
44	2	N5	+	o	+	+
45	2	N6	+	o	+	o
46	2	N7	+	o	+	+
47	2	N8	+	o	+	+
48	2	N9	+	o	+	+
49	2	N10	+	o	+	o
50	2	NV11				
51	2	NV12	o	o	o	o

1)\* for positive layers

2)\* for negative layers

Table 3 shows that correspondingly good values as in Table 2 were obtained for the electrochemically post-treated supports, and in particular the values for the zincate test were further improved.

- 5        In addition to the tests described above, which were carried out with all the supports, supports prepared according to Examples 1 to 3 of Table 2 were also coated, as described under D1, with a positive-working light-sensitive layer, and printing forms were  
10       prepared by exposure and development. With these, printing tests were carried out which gave up to 210,000 perfect prints. A printing form which was prepared analogously with a support from comparison example NV12 (Table 2) showed poorer roll-up behavior.  
15       After 170,000 prints, fine halftone dots were no longer correctly reproduced.

WHAT IS CLAIMED IS:

1. A support material for offset printing plates, comprising:
  - an aluminum-containing base material; and
  - a hydrophilic coating applied to at least

5 one side of said aluminum-containing base material, said hydrophilic coating comprising a phosphonic acid compound selected from the group consisting of a polymer of acrylamidoisobutylene phosphonic acid, a copolymer of acrylamide and acrylamidoisobutylene phosphonic

10 acid, a salt of either of the above with an at least divalent metal cation, and combinations of any of the above.
2. The support material as claimed in Claim 1, wherein the acrylamide/acrylamidoisobutylene phosphonic acid monomer ratio of said copolymer and copolymer salt is from about 1:99 to about 99:1.
3. The support material as claimed in Claim 2, wherein said monomer ratio is from about 3:97 to about 90:10.
4. The support material as claimed in Claim 1, wherein said metal cation is selected from the group consisting of a  $V^{3+}$ ,  $Bi^{3+}$ ,  $Al^{3+}$ ,  $Fe^{3+}$ ,  $Zr^{4+}$ ,  $Sn^{4+}$ ,  $Ca^{2+}$ ,  $Ba^{2+}$ ,  $Sr^{2+}$ ,  $Pb^{2+}$ ,  $Co^{2+}$ ,  $Fe^{2+}$ ,  $Mn^{2+}$ ,  $Ni^{2+}$ ,  $Cu^{2+}$ ,  $Zn^{2+}$  and  $Mg^{2+}$  ion.

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5. The support material as claimed in Claim 1, wherein said coating comprises a mixture of at least two of said polymer, copolymer, and salt.
6. The support material as claimed in Claim 1, wherein said aluminum-containing base material has been pickled.

7. The support material as claimed in Claim 1, wherein said aluminum-containing base material has been roughened.

8. The support material as claimed in Claim 1, wherein said aluminum-containing base material has been anodically oxidized.

9. The support material as claimed in Claim 6, wherein said aluminum-containing base material has a peak-to-valley height  $R_z$  of from about 3 to about 10  $\mu\text{m}$ .

10. The support material as claimed in Claim 8, wherein the oxide layer of the aluminum is from about 0.3 to about 3.0  $\mu\text{m}$  thick.

11. The support material as claimed in Claim 9, wherein the oxide layer of the aluminum is from about 0.3 to about 3.0  $\mu\text{m}$  thick.

12. A process for the preparation of a support material for offset printing plates, comprising:

coating an aluminum-containing base material with a phosphonic acid compound as <sup>defined</sup> ~~claimed~~ in Claim 1, said phosphonic acid compound being in the form of an aqueous solution having a concentration of from about 0.2 to about 5.0% by weight; and

drying said base material;

wherein said coating step is performed by dipping or electrochemical treatment.

13. A process as claimed in Claim 12, said process including one or both of the steps of pickling and anodically oxidizing said aluminum-containing base material prior to said coating step.

14. A process for the preparation of a support material for offset printing plates, comprising:

coating an aluminum-containing base material with

- a phosphonic acid compound selected from the group consisting of the polymer and copolymer of Claim 1 and combinations thereof, said phosphonic acid compound being in the form of an aqueous solution having a concentration of from about 0.01 to about 10.0% by weight; treating the coated aluminum-containing base material with a salt solution having a concentration of from about 0.1% by weight to saturation, said salt containing a divalent metal ion selected from the group consisting of a  $V^{5+}$ ,  $Bi^{3+}$ ,  $Al^{3+}$ ,  $Fe^{3+}$ ,  $Zr^{4+}$ ,  $Sn^{4+}$ ,  $Ca^{2+}$ ,  $Ba^{2+}$ ,  $Sr^{2+}$ ,  $Ti^{3+}$ ,  $Co^{2+}$ ,  $Fe^{2+}$ ,  $Mn^{2+}$ ,  $Ni^{2+}$ ,  $Cu^{2+}$ ,  $Zn^{2+}$  and  $Mg^{2+}$  ion, thereby forming a coating of the salt of said phosphonic acid compound; and drying said base material.

15. A process as claimed in Claim 14, wherein said salt solution is aqueous.

16. A process as claimed in Claim 14, wherein said coating step and said treating step include immersing said base material in baths of the respective coating and treating solutions.

17. A process as claimed in Claim 14, wherein said phosphonic acid compound solution has a concentration of from about 0.1% to about 5% by weight, and said salt solution has a concentration of from about 0.5 to about 10% by weight.

18. A process as claimed in Claim 14, wherein said base material is rinsed after said treating step.

19. A process as claimed in Claim 14, wherein said drying step is performed at a temperature of from about 110 to about 130°C.

20. A process as claimed in Claim 14, wherein said process includes one or both of the steps of



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pickling and anodically oxidizing said aluminum-containing base material prior to said coating step.

21. An offset printing plate formed by coating the support material of Claim 1 with a light-sensitive material.

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ABSTRACT OF THE DISCLOSURE

The invention relates to a support material based on aluminum, which carries a hydrophilic coating which is composed of a polymer of acrylamidoisobutyl-  
5 enephosphonic acid, a copolymer of this acid with acrylamide or salts of the polymers with an at least divalent metal cation. The hydrophilized material is used as a support for light-sensitive substances for the preparation of printing plates.